J. Chem. & Cheml. Sci. Vol.1 (4), 249-266 (2011)

Benzylation of Imidazol Under a New Multi – Site Phase – Transfer Catalyst – A Kinetic Study

Varathan Selvaraj[1] and Venugopal Rajendran[2]

[1]Sri Chandrashekarendra Saraswathi Viswa Maha Vidyalaya
Deemed University, Enathur, Kanchipuram - 631561 TamilNadu, India.
[2]Head of The Department of Chemistry Pachaiyappa's College For Men
Kanchipuram, Tamil Nadu - 631 501 India.

ABSTRACT

A new multi-site phase-transfer catalyst viz., 1,3,5,7-tetrabenzylhexamethy lenetetrammonium tetrabromide was prepared from low cost starting materials. The structures of the synthesized MPTC and N-benzyl imidazole were evidenced by H^1 NMR and C^{13} NMR, etc. The potentiality of the new multi – site phase- transfer catalyst was demonstrated by following the kinetics of N – benzylation of imidazole under pseudo – first order conditions by employing aqueous sodium hydroxide and imidazole in excess, and the reaction was monitored by gas Chromatography. Further, the catalytic efficiency of the MPTC was compared with single–site phase- transfers catalysts.

Keywords: Phase-transfer catalysis, Catalytic activity, N-benzylation, Imidazole, Urotropine, Kinetic study, MPTC etc.

INTRODUCTION

In view of the increasing environmental and economical concerns in recent years, it is now essential for chemists to find as many environmentally benign catalytic reaction as possible. For a successful completion of a reaction, involving lipophilic reactant and hydrophilic reactant, it is imperative that the reactants collide with each other as often as possible. One must notice that the use of protic solvent in reactions involving immiscible reactants may enhance the reaction rate. However this is accompanied by unfavorable reaction[1,2]. As a consequence, these techniques are industrially unattractive, constrained and polluting.

A plausible technique now widely known as "Phase-transfer catalysis" (PTC) was developed for overcoming the hindrance due to the mutual insolubility of aqueous phase with organic phase[3-28]. In this approach, the PTC has the ability to carry one of the reactants, residing in immiscible phase, as highly reactive species, penetrate into the other phase for reaction take place. The main advantages of using phase – transfer

catalyst are to obtain a large conversion, high reaction rate and good selectivity at moderate reaction conditions.

Idoux *et al.*[29], first reported the soluble and insoluble phosphonium ion containing multi – site PTCs, which have three active sites. In resent year Wang and Lee reported the efficiency of the catalytic capabilities of quaternary ammonium ions having two active sites used in the investigation of ethoxylation reaction[30,31]. However, not all quaternary salts serve effectively as PTCs [32]. Alkylation reactions have been widely studied and the results contribute significantly to the understanding of the nucleophilic properties of the amide and amine moiety. N- alkylation of primary and secondary amide and amine has been practiced for decades, both in the presence of stoichiometric amounts of strong bases or under phase – transfer conditions[33-36]. Cycloalkylations are important reactions in organic synthesis, and often in pharmaceutical syntheses[37-39].

Amines are widely used as intermediate in the preparation of solvents, fine chemicals, agrochemicals, pharmaceuticals and catalysts for polymerizations. The nucleophilic attack of alkyl halides by primary and secondary amines is useful for the preparation of tertiary amines but the reaction is invariably slow and give rise to a mixture of secondary and tertiary amines [40]. The thermal reaction between alkyl halides and amines in the presence of a base requires a longer reaction time periods and affords lower yield of the desired product. Therefore these methods are limited in view of harsh reaction conditions.

The genesis of the current work lies in these lacunae. As part of an ongoing program, we have decided to design a novel multi – site phase transfer catalyst containing the maximum possible number of active sites. Herein we report, for the first time, the synthesis of tetra quaternary ammonium bromide viz., 1,3,5,7-tetrabenzylhexamethylenetetrammonium tetrabromide, multi – site phase transfer catalyst (MPTC) by a only one step process using inexpensive starting materials **(scheme 1).** The product obtained has been well characterized by spectroscopic techniques such as FT-IR, H^1 NMR and C^{13} NMR, etc. Having successfully designed and synthesized the novel MPTC, we decided to examine its efficiency by studying the kinetics of N –benzylation of imidazole under pseudo – first order reaction conditions **(scheme 2).** This paper reports for the first time a thorough kinetic study of the same by varying different experimental parameters. We have also compared the catalytic efficiency of is newly prepared MPTC with the various single-site phase-transfer catalysts.

2. EXPERIMENTAL

2.1. Materials

Ethanol, sodium hydroxide, imidazole, benzyl bromide, hexamethylenetetramine (urotropine), tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium hydrogensulphate (TBAHS), tetraethylammonium bromide (TEAB), and trioctylmethylammonium chloride ie., Aliqate 336 and other reagents were all guaranteed grade (GR) chemicals, and were used as received without further purification.

2. 2. Synthesis of MPTC

A mixture of 7g of hexamethylenetetramine, 40 mL of benzyl bromide, and 60 mL of ethanol was placed in a 250 mL three necked round – bottomed Pyrex flask. The reaction was carried out at 40°C for 24 hours and was gently refluxed in the nitrogen atmosphere. The solvent was then completely removed under vacuum and onium salt, ie, 1,3,5,7-tetrabenzylhexamethylenetetrammonium tetrabromide (MPTC) was washed with n- hexane (3 x 20 mL). The white solid MPTC was stored in a $CaCl_2$ desiccator. m.p 199°C;Yield: 90%; ^{1}H NMR (100 MH_Z, DMSO); δ.4.06 (s,8H-Ar-CH_2), 5.30 (s,12H, N-CH_2), 7.44-7.77 (m,5H, ArH); ^{13}C NMR (400 MH_Z, DMSO): δ 69.48 (Ar-CH_2), 78.77 (N-CH_2), 128.53, 128.76, 128.90, 129.90. (Ar-C) for hexamethylenetetramine (HMTA) ^{1}H NMR (400MH_Z, DMSO): δ 4.71 (s,12H, N-CH_2); ^{13}C NMR (100 MH_Z, DMSO): δ 76.13 (N-CH_2); MS (EI, 70 Ev, %): M/Z 824; Elemental analysis Calc.: C, 49.51; H, 4.85; N, 6.79; Found, C, 49.47; H, 4.79; N, 6.81.

2.3. Synthesis of N-benzyl imidazole

A mixture of (13.20 mmol) imidazole, (11.69 mmol) benzyl bromide, (10.71 M) sodium hydroxide, (30 mL) chlorobenzene, (5 mmol%) MPTC with respect to limiting reagent, benzyl bromide was prepared at 40^{o}C. The mixture was stirred continuously using a mechanical mixer at 700 rpm. After 3 h of reaction, the two-phase solution was separated and the portion of organic solution was washed five times with distilled water to remove NaOH and MPTC. The organic solvent was removed by vacuum evaporator. Then, the mixture was separated by column chromatography. Yield 90%; the product were identified ^{1}H NMR (400 MH_Z,$CDCl_3$): δ 5.09 ppm (s,2H, CH_2),6.88-6.89 ppm (t,1H, N-CH=N), 7.07 (s,1H, N-CH), 7.13-7.36 (m, 5H, Ar-CH); ^{13}C NMR (400 MH_Z, $CDCl_3$): δ 50.80, 119.33, 127.31, 128.28, 129.01, 129.83, 136.25, 137.47. (Ar-C); MS (EI, 70 Ev, %): M/Z 158; Elemental analysis Calc.: C, 75.94; H, 6.66; N, 17.72; Found, C, 75.91; H, 6.61; N, 17.75.

2.4. Kinetics of the benzylation of imidazole

The reaction was conducted on a 150 mL three-necked Pyrex round-bottom flask which permits agitating the solution, inserting the water condenser to recover organic reactant and taking samples and feeding the reactants. This reaction vessel was suspended at the center of the thermo state. A known quantity of chlorobenzene (30 mL, solvent), sodium hydroxide (10.71 M), 0.5 g biphenyl IS, (internal standard) were introduced into the reactor. Then, 13.2 mmol of imidazole and 11.69 mmol of benzyl bromide, 5 mol % MPTC (with respect to benzyl bromide, limiting reagent) were introduced to the reactor to start the reaction. The reaction mixture was stirred at 700 rpm. The phase separation was almost immediate on arresting the stirring process. Samples were collected from the organic layer of the mixture (by stopping the stirring for 20-30 seconds each time) at regular time intervals. A pinch of anhydrous $CaCl_2$ was placed in the sample vials to absorb any moisture present in the organic layer. Each run consisted of six samples taken over the period ranging from 5 to 30 minutes. The kinetics was followed by estimating the

amount of benzyl bromide (limiting reagent) that disappeared using a gas Chromatography (GC-Shimadzu 17A model). The analyzing conditions were as follows; Column, 30 m x 0.525 mm i.d. capillary column containing 100% poly(dimethl siloxanen); injection temperature, 250^0C; FID detector (300^0C). Yields were determined from standard curve and using biphenyl as internal standard.

2.5 Reaction and mechanism

This paper describes, the non-benzonoid aromatic nucleophilic substitution reaction between imidazole and benzyl bromide, was employed in the presence of MPTC (QBr).The rate of the reaction is discussed in section 3. The reaction mechanism is represented in **Scheme 2.**

2.6. Definition

The conversion (X) of benzyl bromide (BzBr) is defined as follows;

$$X = 1- [BzBr]_o/[BzBr]_{o,t} \quad (1)$$

Where $[BzBr]_o$ and $[BzBr]_{o,t}$ represent the concentration of benzylation at time (t), $t = 0$ and $t > 0$, respectively.

2.7. Rate expression

The rate expression for this reaction may be expressed as:

$$-r_{(BzBr)} = k_{app} [BzBr]_o \quad (2)$$

Were k_{app} is the apparent reaction rate constant.

$$-d [BzBr]_o / dt = -r_{(BzBr)} = k_{app} [BzBr]_o \quad (3)$$

This reaction is carried out in a batch reactor, so the diminution rate of [BzBr] with time (t) can be expressed on integrating the Eq.(3):

$$-\ln [BzBr]_o/[BzBr]_{o,t} = -\ln (1-X) = k_{app}\, t \quad (4)$$

Using Eq.4, we can get k_{app} value experimentally by plotting –ln(l-X) against time, t.

3. RESULTS AND DISCUSSION

Having successfully synthesized a new multi – site phase transfer catalyst, MPTC we ascertained the effect of several experimental parameters that control the catalytic activity of the MPTC, by choosing the N-benzylation of imidazole with benzyl bromide as a model reaction **(scheme 2).** The kinetic experiments were conducted under pseudo – first order conditions with excesses of aqueous sodium hydroxide and imidazole. The kinetics of N- benzylation was followed by estimating the amount of benzyl bromide that disappeared using gas Chromatography. The pseudo-first order constants were evaluated from the plots of -In (1-X) versus time, where X is the concentration of benzyl bromide at any time (t).

3.1. Effect of change of agitation speed

The essential condition for a reaction to occur is the effective collision of reactant molecules, even in the phase-transfer catalysis system. To ascertain the influence of stirring speed on rate of the reaction, we varied the speed of agitation from 200 rpm to 1000 rpm in the presence of MPTC as the catalyst under pseudo-first

order reaction conditions at 40^0C (Fig.1). The apparent rate constants are evaluated from the linear plots of -In (1-X) versus time. The results indicate that the rate of the reaction increases linearly as the agitation speed increases from 200 to 700 rpm. This is because the interfacial area per unit volume of dispersion increases with the corresponding increase in the stirring speed. The increase of the stirring speed changes the particle size of the dispersed phase. Therefore, in order to study the other kinetic variables of benzylation of imidazole we kept the stirring speed at 700 rpm. Above 700 rpm, there is no significant change in the apparent rate constant. Hence, Fig. 1 is indicative of an interfacial reaction mechanism[41-42] rather than of a Starks extraction mechanism. Chiellini *et al*.[43] reported that the continuous increase in the rate of ethylation with stirring speeds up to 2000 rpm; proceed through an interfacial mechanism. Wang *et al*.[44] and Murugan *et al*.[45] observed a continuous increase in the rate of ethylation of phenylaceto nitrile (PAN), for which an interfacial mechanism was proposed.

3.2. Effect of Varying Substrate Concentration

The amount of benzyl bromide was varied from 1.69 mmol to 18.31 mmol while keeping imidazole at 13.2 mmol and NaOH at 10.3142M. The apparent rate constant increases as the amount of BzBr increases (Table. 1). The increase in the rate may be attributed to the proportionate increase in the number of catalytic active sites available in the MPTC. When the BzBr concentration was increased, the probability of finding the substrate along with active-site of the catalyst is enhanced and thereby the rates of reaction increased. This result suggests that the concentration of BzBr in the organic phase is higher and that the concentration of the substrate at the interface may be essential. Recently, Wang *et al*[46]. observed a similar trend for the N-alkylation of succinimide with 1-bromo-3-phenyl propane using TOAB as PTC.

3.3 Effect of amount of catalyst.

The effect of the amount of MPTC catalyst on the reaction was studied by conducting six experiments. As show in Fig.2 the apparent rate constant (k_{app}) is plotted against the MPTC amount ranging from 2.5 to 30 mol%. with respect to BzBr. It is obvious that the apparent rate constant (k_{app}) increased linearly with the amount of MPTC. In the absence of MPTC 6% of the conversion of benzyl imidazole was obtained after 3hr. Nevertheless, 40 % of the conversion was obtained only within 15 min of reaction when 5 mol% of (MPTC) catalyst was added to the solution. It shows that the phase – transfer catalyst is indeed capable of promoting the benzylation of imidazole effectively. In the kinetics study of the ethylation of P- chlorobenzene under PTC condition, Wang and Rajendaran[47] observed a similar dependence of pseudo-first order constant on the amount of catalysts.

3.4 Effect of Quaternary Ammonium Salts.

Quaternary ammonium salts are generally used as phase-transfer catalysts to promote reaction rate. In addition to MPTC, six other single site quaternary ammonium

salts, such as tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium hydrogensulphate (TBAHS), tetraethylammonium bromide (TEAB), and trioctylmethylammonium chloride ie., Aliqate 336, were investigated to test their reactivities. The experimental result are listed in Table 2. The reactivity of the imidazole anion, depends on its degree of hydration and on the structure of its counter cation. A comparison among TEAB, TBAB, and TBAB reveals that the more lipophilic of the quaternary ammonium cation, the greater the effectiveness in transferring nucleophilic anion into the organic media. In other words, the catalytic activities are mainly due to the solubilities of their ion-pair $Q^+ N^-$ in the organic phase, which turn can be attributed to the nature and bulkiness of Q^+ and the medium. As shown in Table 2, the reactivities of TBAB, TBAC, and TBAHS are not affected significantly by the anions X^-, with the symmetric tetrabutyl ammonium cation (Q^+). However, the sulfate ion of TBAHS catalyst is relatively weaker in basicity than those of Br^- and Cl^- of TBAB and TBAC catalysts. Therefore, the dissociation of HSO_4^- from TBAHS is more difficult than those of TBAB and TBAC catalysts. For this, the reactivity of TBAHS is less than those of TBAB and TBAC catalysts. The activity of the lipophilic cation Q^+ is determined mainly by two factors: its extractability and the anion activation ability, Structural factors affect the formation of active catalyst cation-anion pairs between the organic phase and aqueous phase. Based on the above argument, the order of the reactivities of these quaternary ammonium salts are in the order MPTC >aliquat 336>TBAB > TBAC >TBAHS>TEAB. Therefore the reaction rate of TBASH is less then these of TBAI, TBAB and TBAC catalysts[48].

3.5 Effect of Varying Sodium Hydroxide Concentrations

In phase-transfer catalytic reaction by quaternary ammonium salt, it is seen that the reaction rate was highly affected by alkaline concentration. The rate of N-benzylation of imidazole strongly depends on the strength of the sodium hydroxide. Kinetic experiments were carried out, employing arrange of 8.25 – 25.00 M aqueous sodium hydroxide under similar reaction conditions. The kinetic profile of the reaction is obtained by plotting –ln (1-X) vs time. The observed rate constants tremendously increased with increase in basicity of hydroxide ion i.e., the apparent rate constants were found to increase with an increase in sodium hydroxide concentration (Fig.3). The main reason is that on increasing the concentration of alkali, the hydroxide ion is less solvated by water molecules i.e. the hydration of OH^- is minimized and as result the activity of OH^- increased. Therefore, at higher alkaline concentration the rate of N-benzylation is much higher than that at low concentration of NaOH. Chillni *et al.*[43] reported that the rate of ethylation of phenyl acetonitrile (PAN) with TBAB increased at higher concentration of hydroxide ion and have proposed an interfacial mechanism. In the study of phenoxide allylation in a phase transfer catalytic system Wu and Lai[49,50] observed that the extraction of phenol (using PTC) is more effective if the base concentration is higher.

3.6 Effect of Temperature

The effect of temperature on rate of reaction between imidazole and benzyl bromide was studied under other wise similar conditions. The temperature was varied from 30 to 50^{o}C . The conversion of benzyl bromide was observed to increase with increase in reaction temperature. The effect of temperature on conversion of benzyl bromide is given in Fig 4. The Arrhenius plot was made to determine the apparent energy of activation (E_a) It was found to be 48.09 kJ. mol^{-1}. K^{-1} (Fig.5). The other thermodynamic parameters namely entropy of activation($\Delta S^{\#}$), enthalpy of activation($\Delta H^{\#}$), and free energy of activation($\Delta G^{\#}$) were calculated from Eyring's equation and the obtained values were -104.69 kJ. K^{-1}. mol^{-1}, 50.98 kJ. K^{-1}. mol^{-1}, 93.75 kJ. K^{-1}. mol^{-1}. respectively. A higher E_a value of 88.58 kJ.mol^{-1}.K^{-1} has been reported for the polystyrene bound trimethylammonium ion catalysed reaction, which was controlled by strict intrinsic reactivity under triphase conditions[51]. Ford *et al.*[52] also reported that the activation energy for heterogeneous ethylation of polyacetonitrile was 82.4 kJ. K^{-1}. mol^{-1} and proposed an interfacial mechanism. The E_a value for the alkylation of pyrrolidine-2-one under solid/liquid PTC in presence of potassium carbonate was reported to be 51.08 kJ. K^{-1}. mol^{-1} and an interfacial mechanism was proposed[53]. In a comprehensive study of the synthesis of 4-bromophenyl allyl ether[51], it has been observed that the conversion of allyl bromide increases with increase of temperature and the value of E_a was found at 51.5 kJ.K^{-1}. mol^{-1}. Yadav *et al.*[54] reported an E_a value of 57.68 kJ.K^{-1}. mol^{-1} , for the etherification reaction between β-napthol and benzyl chloride in the presence of NaOH and tetrabutylammonium bromide (TBAB). In the present investigation, it is proposed that the reaction proceeds through interfacial mechanism.

3.7. Effect of the Organic Solvents

In the phase-transfer catalytic reaction, the solvent dramatically influences the reactivity. Dibutly ether, toluene, benzene, chlorobenzene, 1,4-dioxane, cyclohexane, were used to investigate the influence of organic solvent on reactivity. The result are shown in Table 3. The order of the reactivities for theses organic solvent was; cyclohexane < 1,4-dioxane < Benzene < Toluene < Dibutyl ether < Chlorobenzene. In the reaction system, organic solvent is used to dissolve the catalyst and benzyl bromide. How ere, the active catalyst and the reacting molecules in the solution often become inactive because they are always surrounded by a number of solvent molecule. In general, the more polar the solvent, the more it can strip the bound water away from the catalyst. High solvation to the active catalyst and reacting molecules often has a negative effect on the acceleration of benzylation. Furthermore, organic solvent also affect the distribution of the active catalyst between the two phases and the chemical environment of the reaction system. The effect of organic solvents on the reaction is complicated. It is not simple to predict their effects simply by using dielectric constant values only.

4. PHASE-TRANSFER MECHANISM STUDY

Generally in the interfacial mechanism[52] of hydroxide ion initiated benzylation under PTC conditions, the hydroxide ion deprotonates the organic substrate N-H at the interface forming an ion-pair, [Na+ N^-], on the addition of the phase-transfer catalyst (Q^+ X^-), ion exchange takes place at the interface there by facilitating the migration of the newly formed ion-pair (Q^+ N^-) easily into the organic phase. This ion-pair reacts with the benzyl ting agent in the organic phase affording N-benzyl imidazole (scheme 2). The role of phase transfer catalyst in the N-benzylation is to enhance the N^- formation at the interface. In a systematic kinetic study[43] of ethylation of PAN, it was reported that the chemical reaction is not the sole rate – determining steps. From the observed experimental results, it is apparent that the dependencies of the kinetic data on the entire stirring speed range, concentrations of the catalyst, aqueous hydroxide ions, temperature and higher E_a value are consistent with the interfacial mechanism. The mechanism of the benzylation of imidazole with benzyl bromide, under MPTC conditions is presented in **scheme 3.**

Table 1
Effect of the variation of substrate amount on the apparent rate constant (k_{app})[a)]

Benzyl bromide (mmol)	k_{app} x 10^{-3}, min^{-1}
1.69	3.56
5.01	4.32
8.35	5.76
11.69	6.59
15.03	7.88
18.31	9.04

a) Reaction conditions: 13.20 mmol of imidazole, 10.71 M sodium hydroxide, 5 mol % of MPTC, 30 mL of chlorobenzene, 700 rpm, and 40^0C.

Table 2.
Effect of the phase-transfer catalysts (PTC) on the apparent rate constant (k_{app})[a)]

PTC	k_{app} x 10^{-3}, min^{-1}
TEAB	3.32
TBAHS	4.49
TBAC	4.65
TBAB	4.77
Aliquat 336	5.04
MPTC	6.59

[a)] Reaction conditions: 11.69 mmol of benzyl bromide, 13.20 mmol of imidazole, 10.71 M sodium hydroxide, 30 mL of chlorobenzene, 700 rpm, and 40^0C.

Table 3.
Effects of the organic solvents on the apparent rate constant (k_{app})[a)]

Organic solvent	polarity (ε)	k_{app} x 10^{-3}, min^{-1}
Cyclohexane	2.1	2.76
1,4-Dioxane	2.3	2.96
Benzene	2.4	2.98
Toluene	2.5	3.26
Dibutyl ether	2.9	3.58
Chlorobenzene	5.7	6.59

[a)] Reaction conditions: 11.69 mmol of benzyl bromide, 13.20 mmol of imidazole, 10.71 M sodium hydroxide, 5 mol % of MPTC 700 rpm, and 40^0C, ε is polarity of the solvent (s).

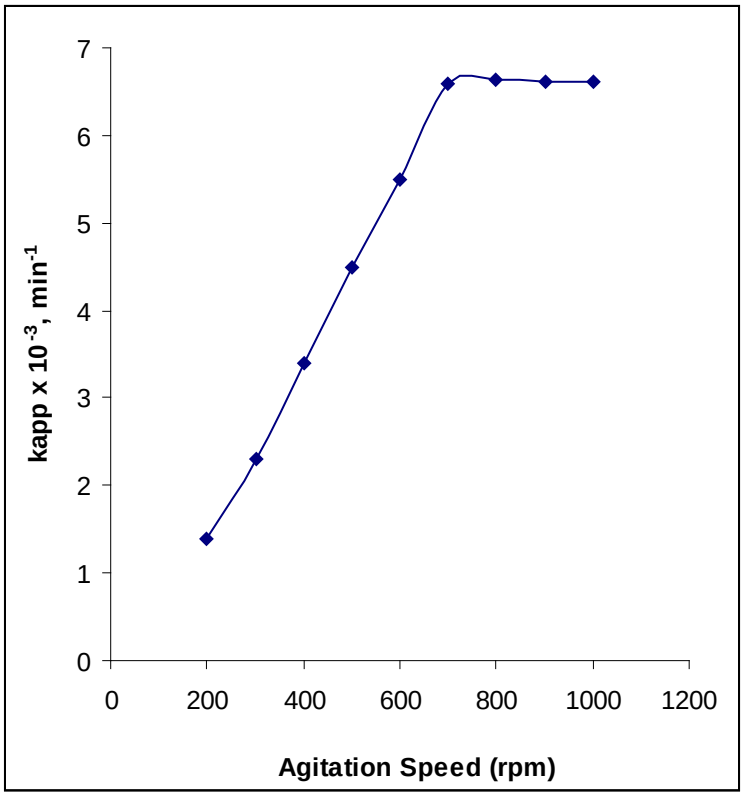


Figure 1

Dependence of k_{app} on agitation speed: 13.20 mmol of imidazole, 11.69 mmol of benzyl bromide, 10.71 M sodium hydroxide, 5 mol% of MPTC, 30 mL of chlorobenzene, at 40^oC.

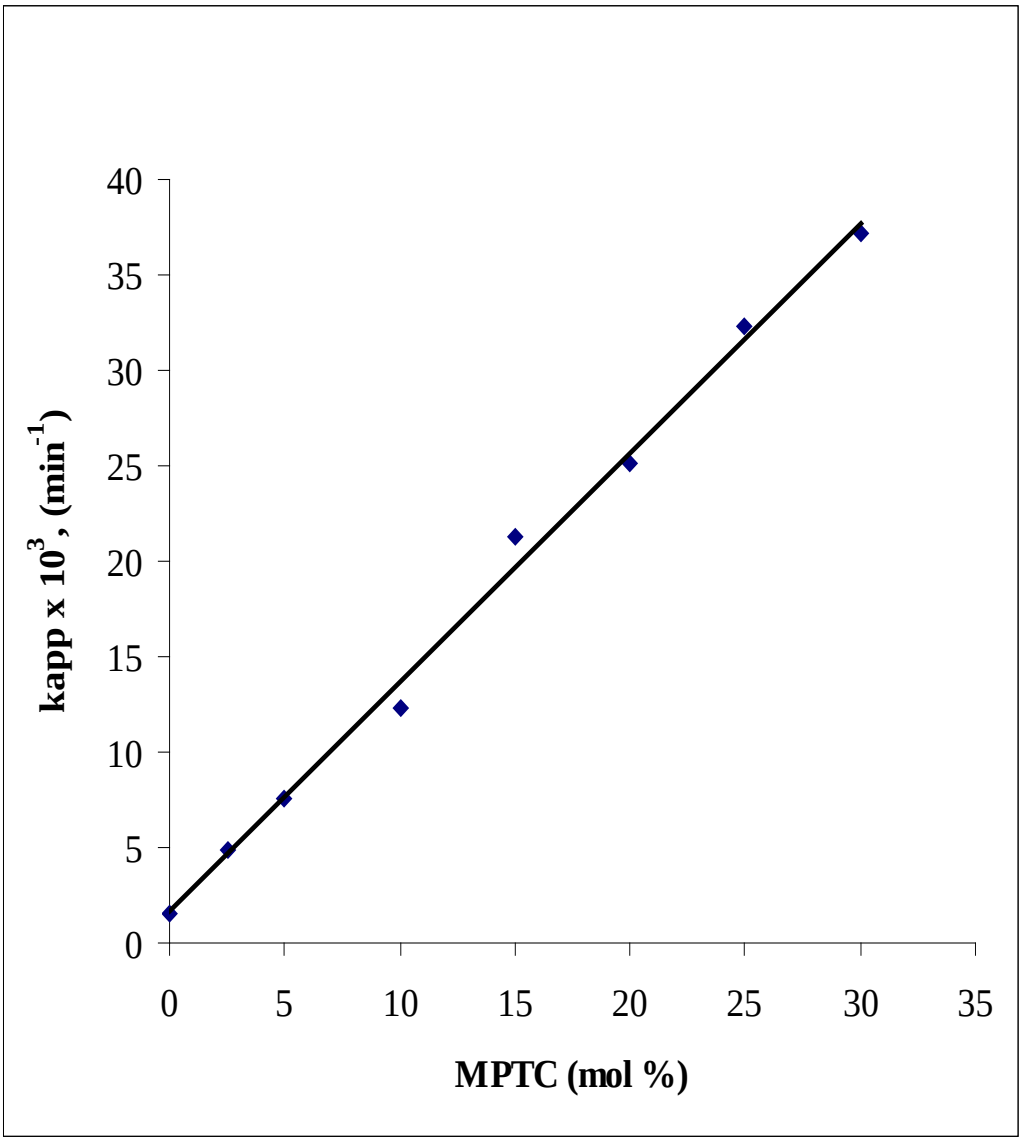


Figure 2

Effect of the amount of MPTC catalyst on the apparent rate constant, k_{app}; 13.20 mmol of imidazole, 11.69 mmol of benzyl bromide, 10.71 M sodium hydroxide, 30 mL of chlorobenzene, 40^{o}C, at 700 rpm.

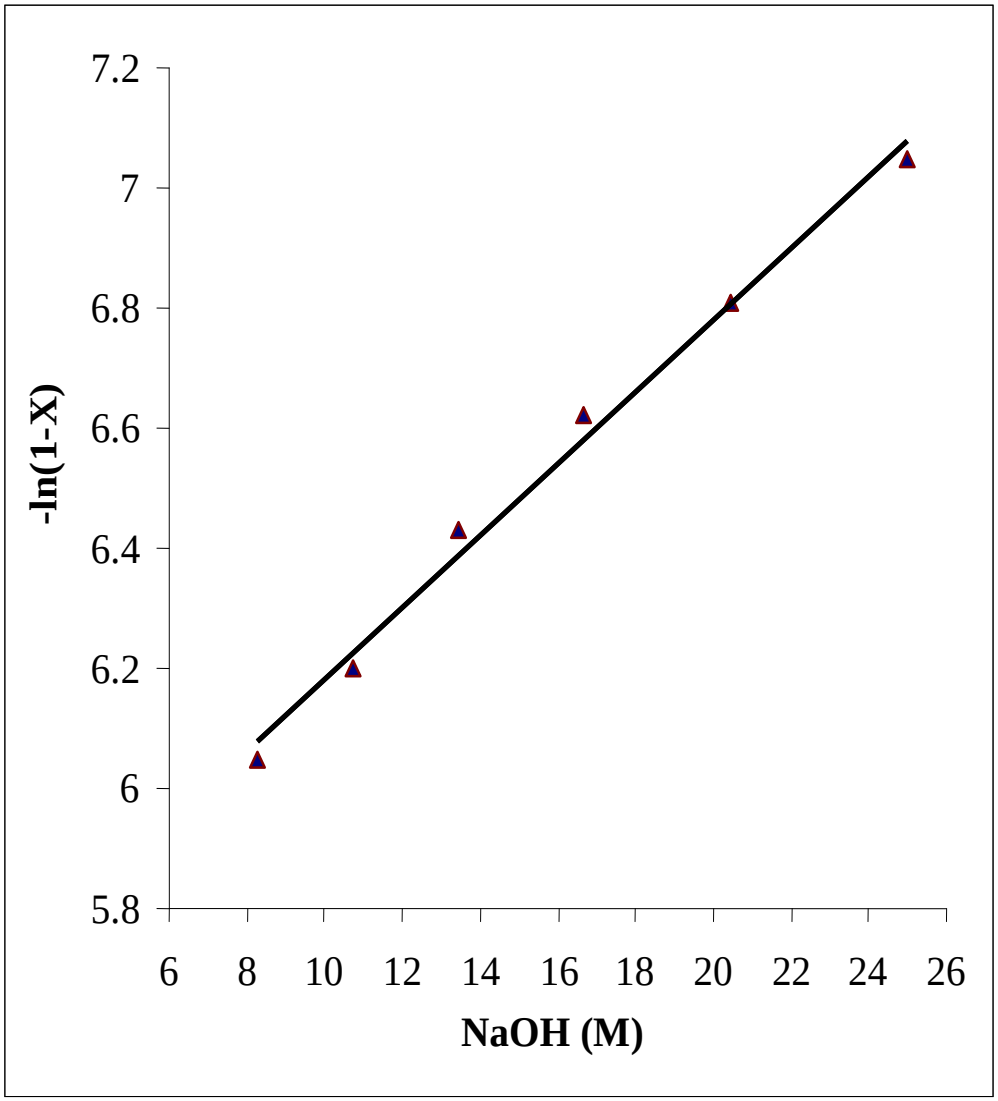


Figure 3

Effect of the Sodium hydroxide on the conversion of benzyl bromide; 13.20 mmol of imidazole, 11.69 mmol of benzyl bromide, 5mol % of MPTC, 30 mL of chlorobenzene, 40^{o}C at 700 rpm.

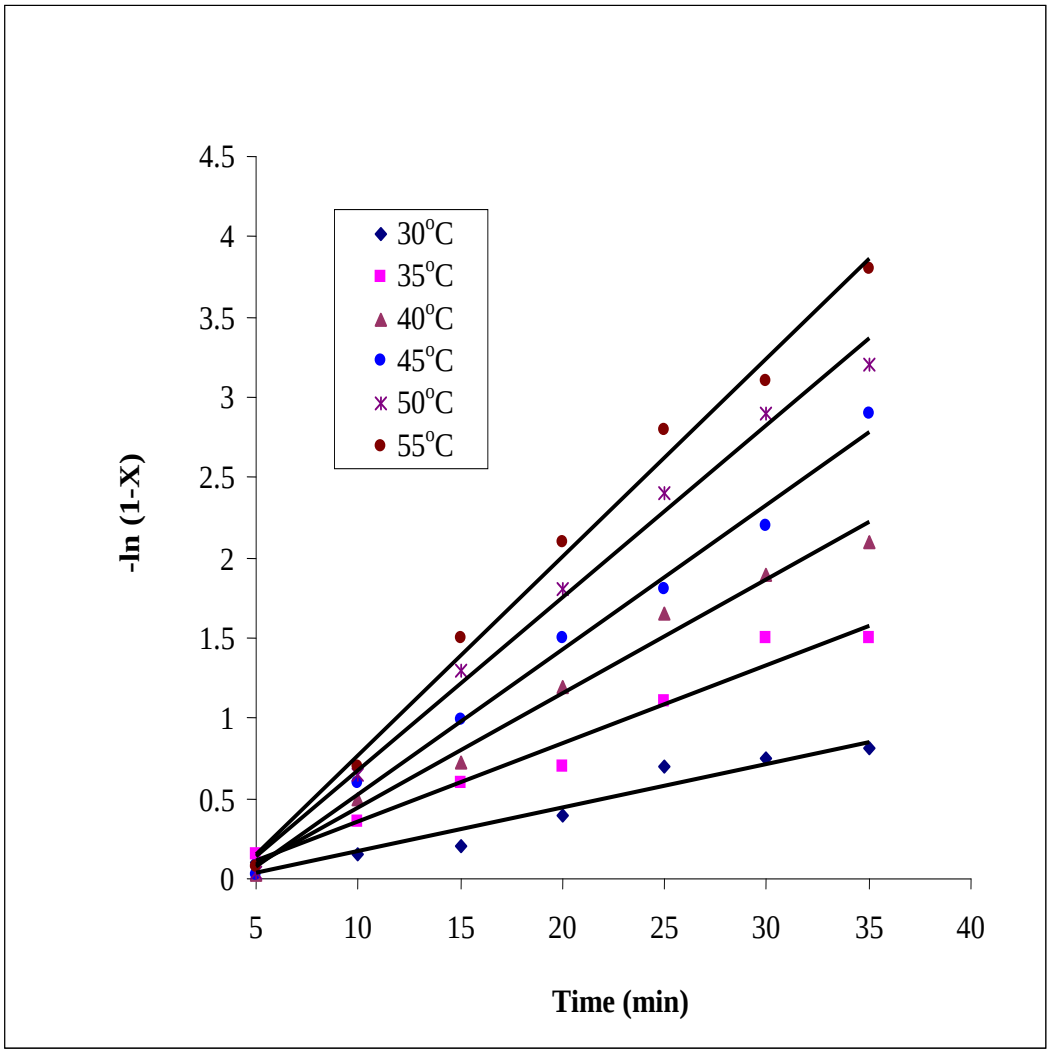


Figure 4

Effect of the temperature on the conversion of benzyl bromide; 13.20 mmol of imidazole, 11.69 mmol of benzyl bromide, 10.71 M sodium hydroxide, 5 mol % of MPTC, 30 mL of chlorobenzene, at 700 rpm.

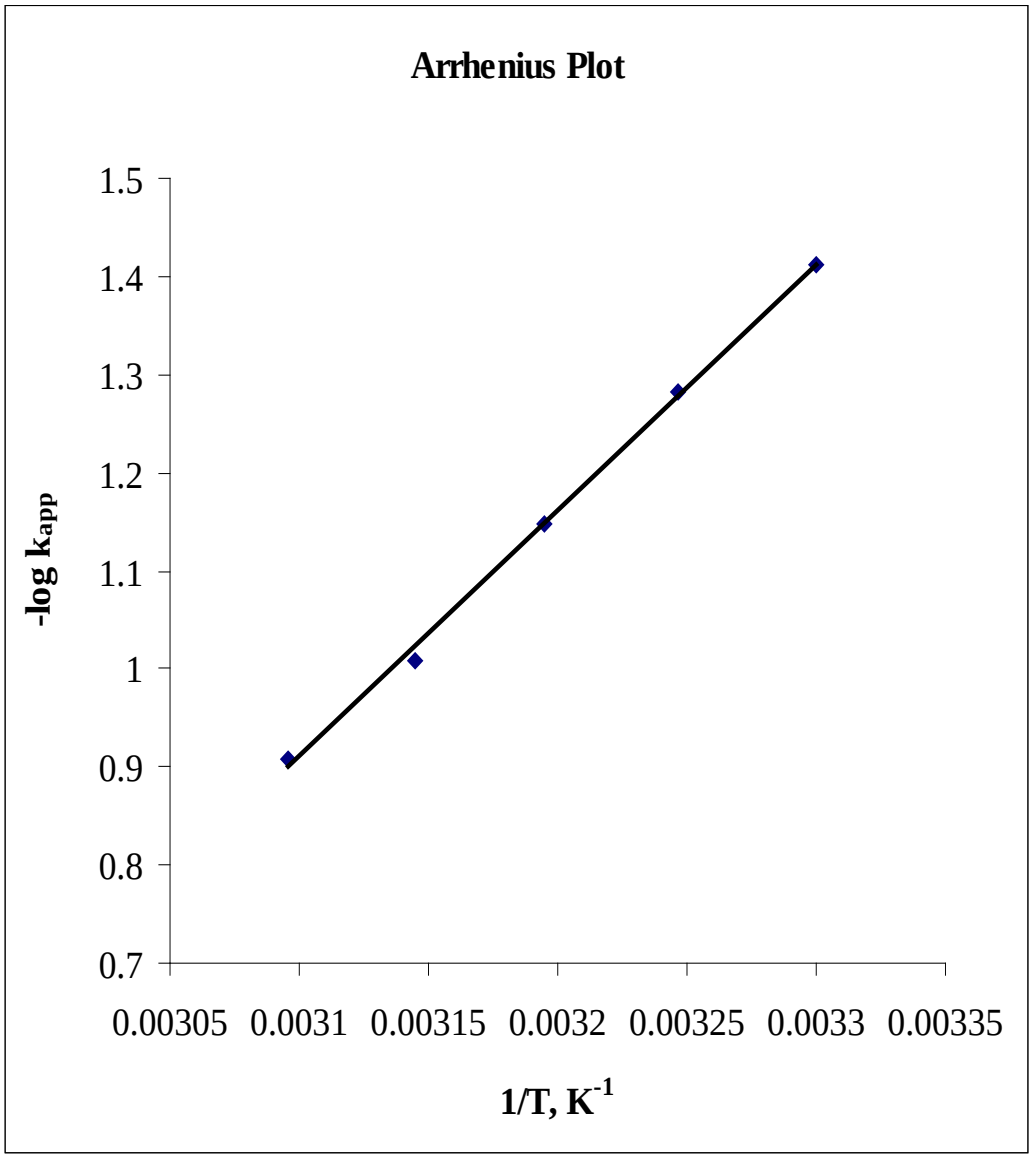
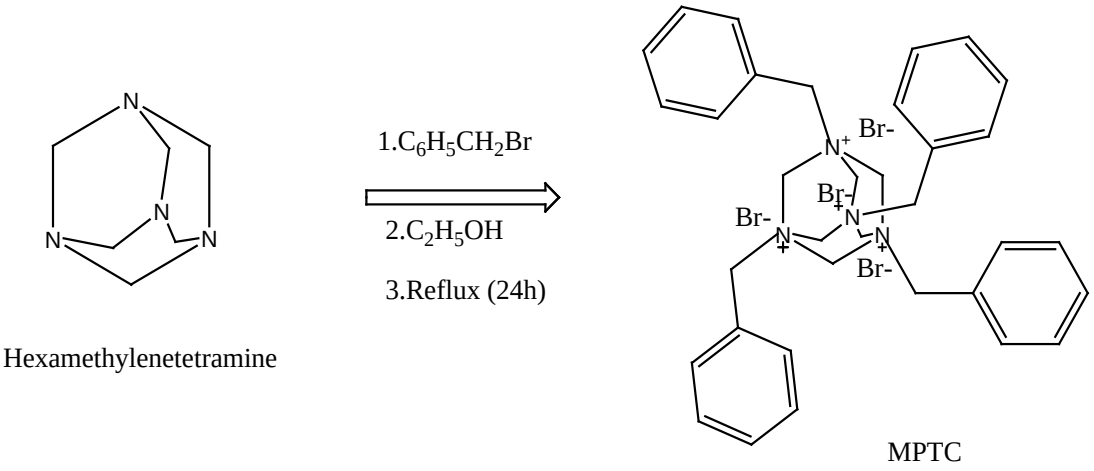


Figure 5

Effect of the Arrhenius Plot on the conversion of benzyl bromide; 13.20 mmol of imidazole, 11.69 mmol of benzyl bromide, 10.71 M sodium hydroxide, 5mol % of MPTC, 30 mL of chlorobenzene.

Scheme - 1

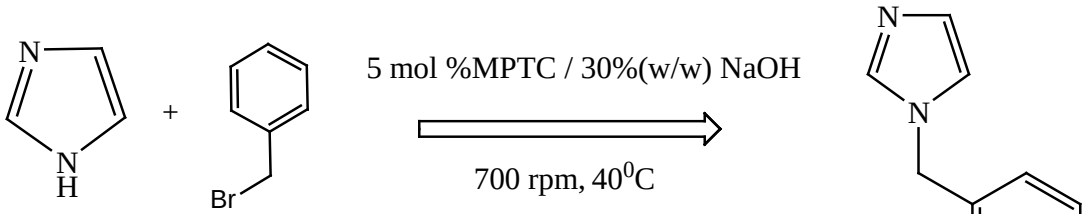


Hexamethylenetetramine

MPTC

MPTC = 1,3,5,7- Tetrabenzylhexamethylenetetramonium tetrabromide

Scheme - 2



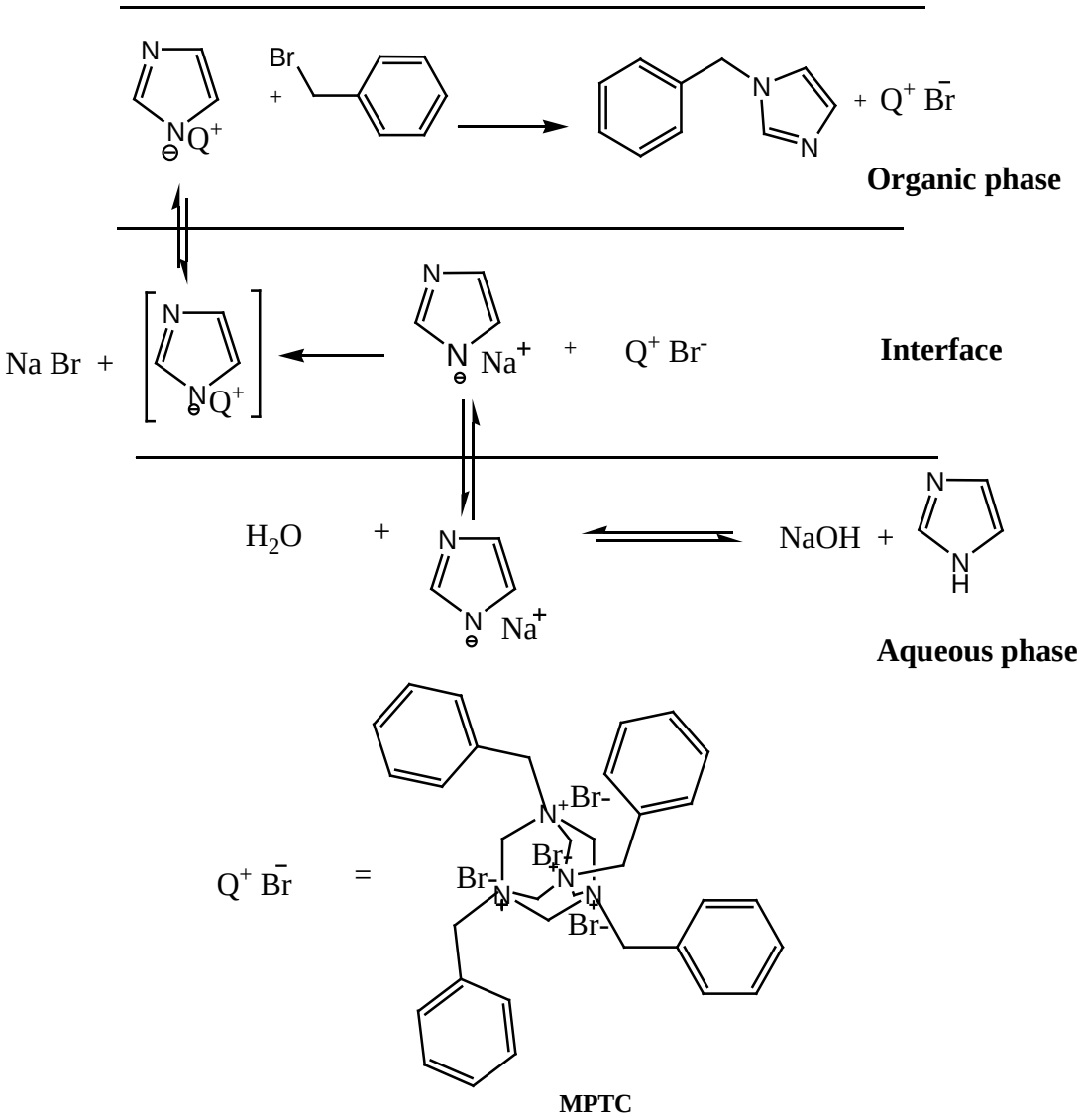
Imidazole

Benzylbromide

N-Benzylimidazole

Scheme 2. Benzylation of imidazole in the presence of MPTC

Scheme – 3



MPTC = 1,3,5,7- Tetrabenzylhexamethylenetetramonium tetrabromide

CONCLUSION

For the first time, we have synthesized and characterized a new multi-site phase transfer catalyst containing four-active-sites (MPTC) and its catalytic ability has been proved thoroughly based on the enhanced pseudo-first order rate constant of benzylation of imidazole with benzyl bromide in the presence of a aqueous

sodium hydroxide(30%,w/w). It is further confirmed that this MPTC is found to be more active than the corresponding soluble four-site MPTC and single-site PTCs owing to higher degree of organophilicity. The change of various experimental parameters, viz., stirring speed, [substrate], [catalyst], [hydroxide ion] have found to influence the observed rate constants in the benzylation reaction even under lower [MPTC] and [NaOH] conditions. Further more, we have also evaluated E_a and other thermodynamic parameters like E_a = 48. 09 kJ. $mol^{-1}.K^{-1}$, $\Delta G^{\#}$ = 93.75 kJ. mol^{-1}. K^{-1}, $\Delta S^{\#}$ = -104.69 e.u and $\Delta H^{\#}$ = 50.98 kJ. $mol^{-1}.K^{-1}$, the observed higher E_a value has confirmed that benzylation reaction should proceed via an interfacial mechanism.

ACKNOWLEDGMENT

The authors would like to thank the Pachaiyappa's Trust, Chennai, Tamil Nadu, India-600 030 and Sri Chandrashekarendra Saraswathi Viswa Maha Vidyalaya, Deemed University, Enathur, Kanchipuram, Tamil Nadu, India, -631 561, for their grant of permission to do this research work.

REFERENCES

1. P.T. Anastas, M.M. Kirchhoff, *Acc. Cheme. Res.* 35, 686 (2002).
2. F.M. Menger, *Chem. Soc. Rev.* 1, 229 (1972).
3. C.M. Starks, *J.Am. Chem. Soc.* 93, 195 (1971).
4. C.M. Starks, C.L. Liotta, M. Halpern, Phase Transfer catalysis, Fundamentals, Applications and Industrial Perspectives, Chapman & Hall, New York, USA, (1994).
5. H.H. Freedman, Industrial Applications of Phase Transfer catalysis (PTC): Past, *Present and Future, Pure Appl. Chem.* 58, 857 (1986).
6. E.V. Dermot, S.S. Dehmlow, Phase Transfer catalysis, VCH Publishers, Weinheim, Germany, (1993).
7. M. Halpern (Ed.), Phase -Transfer catalysis, Mechanisms and Syntheses, *American Chemical Society, Washington, DC, USA* (1997).
8. W.P. Weber, G.W. Gokel, Phase Transfer catalysis, in organic Synthesis Reactivity and Structure Concepts in organic Chemistry, Vol. 4, Springer-Verlog, Berlin, Heidelberg, (1997).
9. Y. Sasson, R. Neumann (Eds.), Handbook of Phase Transfer catalysis, Chapman & Hall, London, UK, (1997).
10. R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, *Chem. Rev.* 91, 1721 (1991).
11. J.P. Jayachandran, M.L. Wang, *Appl. Catal.A: Gen.* 198, 67 (2000).
12. M.L. Wang, in: Y. Sasson, R. Neumann (Eds.), Handbook of Phase Transfer-catalysis, Blackie Academic & Professional, London, (1997).
13. Y.C. Fiamegos, C.D. Stalikas, *Anal. Chin. Acta* 550, 1 (2005).
14. M. Makosza, *ACS Symp. Ser.* 695, 41 (1996).
15. M.A. Harmer, Q. Sun, *Appl. Catal. A: Gen.* 221, 45 (2001).
16. G.D. Yadav, S.V. Lande, *Appl. Catal. A: Gen.* 287, 267 (2005).

17. C.C. Huang. H.M. Yang, *Appl. Catal. A: Gen.* 290, 65 (2005).
18. S. Baj, A. Siewniak, B. Socha, *Appl. Catal. A: Gen.* 309, 85 (2006).
19. T. Balakrishnan, E. Murugan, A. Siva, *Appl. Catal. A: Gen.* 273, 89 (2004).
20. N. Taha, Y. Sasson, M. Chidambaram *Appl. Catal. A: Gen.* 350, 217 (2008).
21. D. Albanes, *Catal. Rev.* 45, 369 (2003).
22. J.J. Jwo, *Catal. Rev.* 45, 396 (2003).
23. H.M. Yang, H.S. Wu, *Catal. Rev.* 45, 463 (2003).
24. D. Albanese, D. Landini, A. Maia, M. Penwo, *J. Mol. Catal. A: Chem.* 150, 113 (1999).
25. S.D. Naik, L.K. Doraiswamy, *AIChE Journal*. 44, 614 (1998).
26. T. Balakrishnan, J.P. Jayachandran, Multisise Phase Transfer Catalyst for organic transformation, *ACS. Symp. Ser*. 659, 277 (1997).
27. G.D. Yadav, S.V. Lande, *Adv. Synth. Catal*. 347, 1235 (2005).
28. M. Makosza, *Pure Appl. Chem.* 72, 1399 (2000).
29. J.P. Idoux, R. Wysocki, S.Young, J. Turcot, C. Ohlman, R. Leonard, *Synth. Commun.*13, 139 (1983).
30. M.L. Wang, Ze-Fa Lee, *Ind. Eng. Chem. Res.* 45, 4918 (2006)
31. J. Bender, D. Jepkens, H. Husken, *Org. Proc. Res & Dev.*, 14, 716 (2010)
32. G.D. Yadav, N.M. Desai, *J. Mol. Catal. A: Chem.* 243, 278 (2006).
33. M. Benaglia, M. Cinquini, F. Cozzi, G. Tocco, *Tetrahedron Lett.* 43, 3391 (2002).
34. S. Jew, B. Jeong, M. Yoo, H. Huh, H. Park, *Chem. Commun.* 14, 1244 (2001).
35. R. Chinchilla, P. Mazon, C. Najera, *Tetrahedron-Asymmetry*.13, 927 (2002).
36. H. Park, B.S. Jeong, M.S. Yoo, J.H. Lee, B.S. Park, M.G. Kim, S.S. Jew, *Tetrahedron Lett.*44, 3497 (2003).
37. J. P. Jayachandran, C. Wgeelet, B.C. Eason, C. A. Eckert, *J. Supercrit. Fluid.* 27, 179 (2003).
38. S.G. Tooh, S.H. Ang, H.K. Fun, C.W. Org, *Organomet. Chem.* 580, 17 (1999).
39. T.S. Basu Baul, A. Mizar, A. Lycka, E. Rivarola, R. Jirasko, M. Holcapek, D.D. Vos, *J. Organomet. Chem.* 691, 3416 (2006).
40. T.E. Muller, M. Beller, *Chem. Rev*. 98, 67 (1998).
41. M. Rabonivite, Y. Sasson, M. Halpern, *J. Org. Chem.* 48, 1022 (1983).
42. H.E.S. Ali, *Catalysis Commun.* 8, 855 (2007).
43. R. Solaro, S.D. Antone, E.G. Chiellini, *J. Org. Chem.* 45, 4179 (1980).
44. J.P. Jayachandran, M.L. Wang, *Appl. Catal.A: Gen.* 319, 19 (2001).
45. E. Murugan, P. Gopinath, *Appl. Catal. A: Gen.* 319, 72 (2007).
46. M.W. Wang, C.J. Chen, *Org. Proc. Res & Dev.* 14 (2010) 734.
47. M.L. Wang, V. Rajndran, *UltraSon. Sonochem.* 14, 368 (2007).
48. M.L. Wang, Y.H. Tseng, *J. Mol. Catal. A: Chem.* 188, 51 (2002).
49. H.S. Wu, J.J. Lai, *Ind. Eng. Chem & Res.* 34, 1536 (1995).
50. M. Rabinoviz. Y. Cohen, M. Halpern, Angew. *Chem. Int. Ed. Engl.* 25, 960 (1986).
51. R.D. Acker, *Tetrahedron Lett.*19, 2399 (1978).

52. M. Tomoi, W.T. Ford, *J. Am. Chem. Soc*. 103, 3821 (1981).
53. Y. Sasson, N. Bilman, *J. Chem. Soc. Perkin Trans.* 2, 2029 (1989).
54. G.D. Yadav, P.M. Bilman, *J. Mol. Catal. A: Chem.* 223, 93 (2004).